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Layered Double Hydroxides intercalated with Chlorine used as low temperature gas sensors

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Abstract

Layered Double Hydroxides (LDHs) are well known class of materials that since their discovery, happened more than one century ago, have been used in a large range of fields (catalysts, drug delivery media, Oxyanion adsorption, etc.). LDHs are characterized by a large Surface/Volume ratio and a strong ability to adsorb molecules of any kind. Even if these two characteristics make it a very good candidate to be a gas sensor, LDHs have not been deeply investigated yet in this direction.
In this work, some evidences of the promising properties of LDHs are shown. In particular, LDHs sensors have been successfully tested in the measuring of three volatile compounds at four different concentrations at room temperature.

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Keywords:

1. Introduction

Since the discovery of the LDHs' first natural phase by Hochstetter in 1842, LDHs have been used in a huge number of applications. Indeed, LDHs have been applied as catalysts, drug delivery media, Oxyanion adsorption, etc. [1, 2]. LDHs, also known as hydrotalcite-like compounds, are a class of ionic lamellar materials belonging to the group of the anionic clays [3]. The general formula may be written as [3, 4]:

$$\left[M^{2+}_{1-x}M^{3+}_{x}(OH)_2\right]_x\left[A^{n-}\right]_{x/n}zH_2O \quad (1)$$

where, in our case, M^{2+} is Zn^{2+}, M^{3+} is Al^{3+} and A^{n-} is Cl^-. LDHs have a lattice structure composed by the stacking of positively charged brucite-shaped layers, consisting of a divalent metal ion M^{2+}, octahedrally surrounded by six $(OH)^-$ hydroxyl groups. The substitution of the M^{2+} metal with a trivalent M^{3+} cation gives rise to the periodic repetition

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of positively charged sheets (lamellas) alternating with charge-counterbalancing A^{n-} ions that allows the electrostatical neutrality of the brucite layers. It is important to highlight that, in the interlayer space, generally are accommodate water molecules and a resultant network of hydrogen bonds between layers. The intercalation ion is an important peculiarity since changing the anion, it is possible to modify the properties of the material (chemical, electronic, optic, etc.) [4] and, in principle, by means the ion substitution, the relative response to the various volatile compounds could be tuned.

LDHs are characterized by a large surface/volume ratio and these structures can adsorb any kind of atoms/molecules, nevertheless, their applications as gas sensors are very limited. In 2006, Morandi et al. [5] calcinated Zn/Al-LDH to obtain ZnO dust for gas detection. In the same way, Xu et al. [6] in 2013 used LDHs as precursors to obtain composite oxides for gas detection. In this paper, the possibility of using LDHs themselves as gas sensors is explored. To this purpose, several resistive sensors based on Zn/Al- LDHs material have been prepared and tested in various atmospheres. The results show that this kind of material is able to detect the tested volatile compounds (CH_4, CO, NO) and discriminate different concentrations at room temperature.

2. Results

Several sensors were prepared growing Zn/Al-LDHs by hydrothermal process on interdigitated fingers to fabricate a variable resistance. The interdigitated substrates were designed and manufactured on standard commercial PCB with golden copper track, 35 µm thick, with the intent of conceiving a device that can be robust and cheap (<50 euro cent per piece). On this structure, a 300 nm thick layer of Al was deposited using a magnetron sputtering DC to trigger the growth mechanism for LDH. The hydrothermal growth of LDHs were carried out by using a nutrient solution composed of a 1:1 ratio of Zinc chloride $ZnCl_2$ and hexamethylenetetramine ($C_6H_{12}N_4$) at 20 mM concentration [7]. Hexamethylenetetramine was used as a pH regulator to control the solution basicity through the hydrolyzation and release of ammonia at high temperature [8]. During the growth, the samples were kept in the middle of the solution bottle, anchored to a 45° tilted glass slide in order to avoid any possible contamination and the growth temperature was fixed at 80°C. After a growth time of 6 hours, the samples were cooled down in ambient atmosphere and then washed with ethanol at room temperature to remove the residuals on the top of the LDH surface. It is important to highlight that the hydrothermal process allows to grow LDHs simultaneously on a very large area and, in this way, it is possible to prepare several sensors at the same time and potentially at very low cost. In figure 1a and b, a sensor and a SEM image of the LDH material grown on the fingers are respectively shown. Figure 1b shows the porous structure of the LDHs.

Figure 1. a) Interdigitated fingers covered by LDH structure. b) SEM image of the LDH structure growth on the interdigitated finger

The prepared sensors were placed in a customized sealed chamber with tube fittings for gas inlet and outlet. The measurements were performed maintaining a constant flux of 200 sccm. The flux was controlled by a mass flow system that sets also the dilution factors of the testing gases. A particular shield, above the sensors, permits a homogenous

distribution of the carrier gas avoiding a direct flow on the sample. Each concentration was obtained diluting in wet air the Nitric Oxide (NO), carbon monoxide (CO) and methane (CH_4) concentrations measured from a certified bottle where they were diluted in pure nitrogen at the concentration of 500 ppm. The sensors were exposed to four increasing concentrations (25, 62, 125 and 250 ppm) of each compound for 60 s and then cleaned in wet air for 500 s. Every volatile compound was measured in triplicate at room temperature. The sensor resistances were collected by an Agilent 34401a multimeter connected to PC.

The variation of the sensor resistance is used as sensor response. Figure 2a shows the measured sensor resistance for two consecutive concentrations (namely 62 and 125 ppm) of CO. Conversely, figure 2b shows the sensor response to the different concentrations of NO, for each measurement, three repetitions are shown. Similar results were obtained for other gases (e.g. CH_4) and the tests were repeated on different samples with very similar behavior. Finally, figure 3 shows the normalized sensor response variation to the different concentrations of the three volatile compounds. The figure shows that sensor response increases almost linearly with the gas concentration. These results clearly show that sensors based on this LDH material are able to detect the three gases taken into consideration and discriminate their concentrations in a wide range.

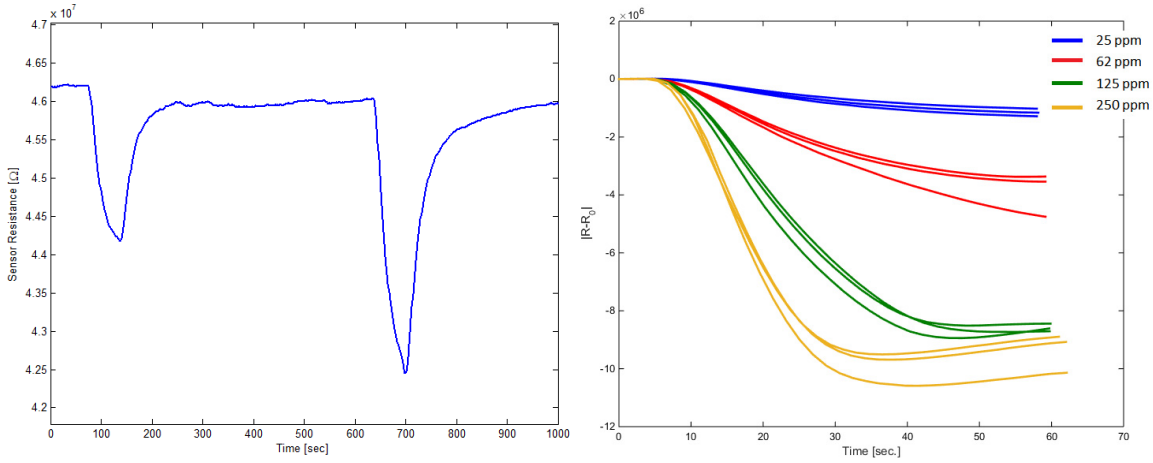

Figure 2: a) Sensor response for two consecutive concentrations of CO (62 and 125 ppm) b) Sensor response for several concentrations of NO diluted in wet air.

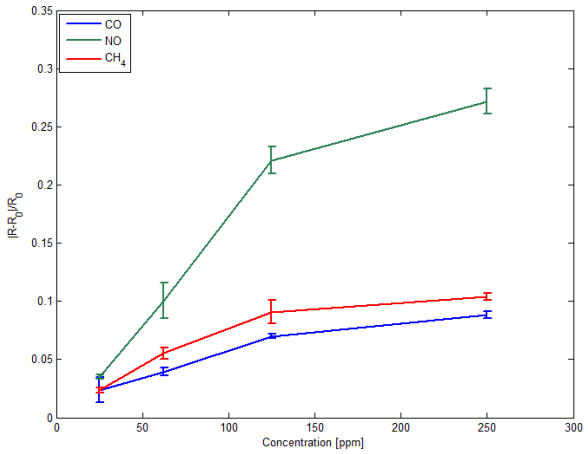

Figure 3: Normalized sensor response variation to several concentrations of CO and CH_4 diluted in wet air. The measurements have been performed in triplicate. The standard deviations are also shown.

3. Conclusions

In conclusion, a gas sensor based on LDH material has been developed. It has been successfully used to detect three volatile compounds (CO, CH_4 and NO) at room temperature. Moreover, the capability of distinguishing several concentrations has been also demonstrated. In future works, the possibility of using this kind of materials to detect other volatile compounds will be investigated in addition to their limit of detection and other sensor characteristics. After an optimization of material including the functionalization with other intercalating ions, this kind of sensors will be compared also with commercial devices.

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